

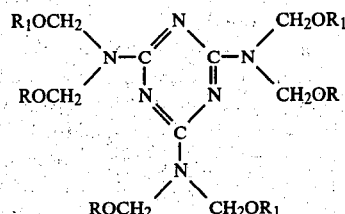
HEAT STABLE, NON-YELLOWING PHOTOPOLYMER COMPOSITIONS

This application is a continuation-in-part of my co-
pending application having Ser. No. 882,021, filed Feb.
28, 1978, now abandoned.

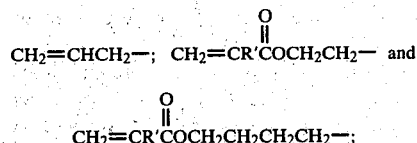
This invention relates to photopolymer compositions.
More particularly, it relates to heat stable, non-yellow-
ing photopolymer compositions.

It is known that polyenes are curable by polythiols in
the presence of free radical generators such as actinic
radiation to solid polythioether-containing resinous or
elastomeric products. See U.S. Pat. No. 3,661,744 and
U.S. Pat. No. 4,008,341. For the most part, however,
these commercially available polyenes and polythiols
used in curing leave something to be desired as far as
heat stability is concerned. This shortcoming was some-
what overcome by the introduction of heat stable poly-
enes derived from hydantoin acids, amines and esters
as set out in U.S. Pat. No. 4,084,020 and two other
polyenes set out in U.S. Pat. No. 3,847,767, both as-
signed to the same assignee. However, although these
materials have good heat stability, their ability to with-
stand discoloration after being heated at high tempera-
tures is negligible.

One object of the instant invention is to provide a
photocurable polyene-polythiol composition which is
substantially non-yellowing after exposure to relatively
high temperature. Another object is to provide a UV
cured coating with good heat stability and non-yellow-
ing characteristics. These and other objects are pro-
vided by a photocurable composition comprising a
polythiol, a photoinitiator and a polyene of the formula:



wherein R are all the same member of the group consist-
ing



R₁ is —CH₃ or R, and R' is —CH₃ or H.

The polyenes per se and their method of synthesis are
old in the art. See for example *Helv Chim Acta* 24, 318
E, (1941); A. Gams, G. Widmer and W. Fisch which
shows a transesterification method of making the allylic
terminated polyene and U.S. Pat. No. 3,020,255 which
teaches a transesterification method of making the
acrylic terminated polyene.

In carrying out these transesterification reactions in
the manner described, complete exchange of the alkoxy
groups is not achieved and is, in fact, not necessary for
the preparation of the polymers of this invention. Thus,
a degree of reaction wherein at least three to nearly six

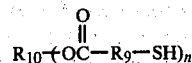
unsaturated alkoxy groups per triazine nucleus is suffi-
cient for the preparation of the non-yellowing photopo-
lymeric coating materials described herein.

Polythiol as used herein refers to simple or complex
organic compounds having a multiplicity of pendant or
terminally positioned —SH functional groups per aver-
age molecule.

On the average the polythiol must contain 2 or more
—SH groups/molecule and have a viscosity range of
essentially 0 to 20 million centipoises (cps) at 70° C. as
measured by a Brookfield Viscometer either alone or
when in the presence of an inert solvent, aqueous dis-
persion or plasticizer. Operable polythiols in the instant
invention usually have molecular weights in the range
about 94 to about 20,000, and preferably from about 100
to about 10,000.

The polythiols operable in the instant invention may
be exemplified by the general formula R₈(—SH)_n where
n is at least 2 and R₈ is a polyvalent organic moiety.
Thus R₈ may contain cyclic groupings and hetero atoms
such as N, P or O and primarily contains carbon-car-
bon, carbon-hydrogen, carbon-oxygen, or silicon-oxy-
gen containing chain linkages.

One class of polythiols operable with polyenes to
obtain essentially odorless polythioether products are
esters of thiol-containing acids of the formula HS-
R₉—COOH where R₉ is an organic moiety with poly-
hydroxy compounds of structure R₁₀(—OH)_n where R₁₀
is an organic moiety and n is 2 or greater. These compo-
nents will react under suitable conditions to give a poly-
thiol having the general structure:



where R₉ and R₁₀ are organic moieties and n is 2 or
greater.

Certain polythiols such as the aliphatic monomeric
polythiols (ethane dithiol, hexamethylene dithiol, deca-
methylene dithiol, tolylene-2,4-dithiol, etc. and some
polymeric polythiols such as a thiol-terminated ethylcy-
clohexyl dimercaptan polymer, etc. and similar polythi-
ols which are conveniently and ordinarily synthesized
on a commercial basis, although having obnoxious
odors, are operable in this invention but many of the end
products are not widely accepted from a practical, com-
mercial point of view. Examples of the polythiol compo-
unds preferred for this invention because of their
relatively low odor level include but are not limited to
esters of thioglycolic acid (HS—CH₂COOH), α-mer-
captopropionic acid (HS—CH(CH₃)—COOH and β-
mercaptopropionic acid (HS—CH₂CH₂COOH) with
polyhydroxy compounds such as glycols, triols, tetra-
ols, pentaols, hexaols, etc. Specific examples of the
preferred polythiols include but are not limited to ethyl-
ene glycol bis (thioglycolate), ethylene glycol bis (β-
mercaptopropionate), trimethylolpropane tris (thio-
glycolate), trimethylolpropane tris (β-mercaptopro-
pionate), pentaerythritol tetrakis (thioglycolate) and
pentaerythritol tetrakis (β-mercaptopropionate), all of
which are commercially available. A specific example
of a preferred polymeric polythiol is polypropylene
ether glycol bis (β-mercaptopropionate) which is pre-
pared from polypropylene-ether glycol (e.g. Pluracol
P2010, Wyandotte Chemical Corp.) and β-mercapto-
propionic acid by esterification.